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FOSSILS AND FOSSILIZATION.

BY L. P. GRATACAP.

(Continued from page 199.)

There are many facts in chemistry which show that there can be mutual displacements in solutions of various substances, although there is also a series of facts that prove the additional solubility of insoluble salts in the presence of other salts or in dilute solutions. Thus, when certain salts, dissolved in a small quantity of water decompose one another by double interchange of bases and acids, producing a precipitate of a difficultly soluble salt, no precipitate occurs in more dilute solutions, although the quantity of water present would not be sufficient to hold in solution the less soluble salt, which may be produced by the decomposition, if it existed in the separate state. For example, sulphate of lime requires about 400 parts of water to dissolve it; but chloride of calcium, dissolved in about 200 parts of water, gives no precipitate with sulphate of potash. It is supposed that the formation of sulphate of lime takes place, but that the presence of the chloride of potassium, which is formed at the same time, renders it more soluble than it otherwise would be. Carbonate of lime seems to be rendered more soluble by the presence of sulphate of potash and chloride of potassium. (Ludwig Gmelin, Hand-book of Chemistry.)

On the other hand we know of the actual displacement of chlorides from solution by other chlorides, as the solubility of chloride of sodium in water diminishes, the greater the amount of chloride of magnesium therein dissolved. Sulphates also affect the relative solubility of the chlorides of sodium and magnesium. In regard to the assumption made here, that silica is driven out as carbonate of lime enters into solution, assuming the structural position of the dissolved carbonate, Bischof says, in his Chemical and Physical Geology (Cavendish Society, Vol. I, p. 199), that "although silica is separated directly from sea water by organic agency, still this separation

may also take place in consequence of a displacement of the sedimentary carbonate of lime and the animal remains contained in it." He further says, "when the carbonate of lime acts as the precipitant to carbonates of magnesia, protoxide of iron and *silica*, in sea water, equivalent quantities of it enter into solution again." All of which can be interpreted as a corroboration of the view given above.

However, the exact method of interchange is described, it can hardly be doubted that the pseudomorphism by which silica assumes the form of crystallized calc-spar is closely or exactly imitated. Von Buch, in his examination of organic silicifications, concluded that the soluble silica deposited from solutions took the place *only* of the organic matter, at least at first, and that the substitution of the silica for carbonate of lime was later, and in this secondary form appeared as warts, concretionary rings, etc. Alexander Petzholdt, in his examination of a silicified belemnite, found that the silicification began on the outside, penetrating progressively through the minute tubes of its structure to the interior, finally effecting a continuous silicification from the inside to the outside. He found the same stages shown in oyster shells; and a section in the center of an oyster shell contained 51.78 per cent. silica and 47.81 per cent. carbonate of lime, with traces of iron oxide, while its exterior was entirely silicified. His observations disproved Von Buch's assumption, and established the fact that the waters carrying silica directly removed the carbonate of lime and so replaced it with opal-material (soluble hydrated quartz), and that no warts, concentric or concretionary rings were formed at all. Whether the replacement by silica of organic tissues, as the structure of wood or the horny apophyses of brachiopods, may involve less obvious conditions than those prevalent in the more ordinary mineral replacement of calcite or aragonite by silica, or not, still the formal character of the substitution is similar. Bischof, in commenting upon this similarity, says, "the penetration of the silicic acid in the minute interspaces of the fibrous carbonate of lime, as also all the appearances presented by the silicified molluscan shells, agree so completely with the penetration of the calc-spar by silicious substances,

and with the entrance of the silica between the cleavage plains of the same, that doubtless we have here one and the same process of alteration. Therein, however, there is a difference between the displacement of the carbonate of lime in the molluscan shell and that in the calc-spar, in so far as the latter is frequently hollow and the former not; in the shell the space of the removed carbonate of lime is entirely, in the calc-spar only partially filled. We might ascribe this difference to the well-known inclination of silicic acid to unite itself with organic substances, if the amount of organic matter were not so small. The true explanation of this difference must await further investigations" (Chemischen and Physikalischen Geologie).

This latter contrast in the silicification of fossils and the pseudomorphism of calc-spar seems to arise principally from contrasted quantitative conditions. The solid replacement of the carbonate of lime in fossils by silica is connected with the former's slow solution, as compared with that of exposed crystallized calcite, which may be rapidly invaded by carbonated or acid waters, whereas the imbedded fossil receives the access of terrestrial waters but slowly, and also retains its carbonate of lime somewhat intermixed with organic envelopes, the sarcodic filaments that penetrate the hard parts of invertebrates, and so surrenders it to solution less quickly, with the result of acquiring a dense and complete molecular replacement. In regard to the view of the solution of carbonate of lime in water expelling its dissolved silica Bischof remarks, that in the case of the hollow crystals of calcite we are shown how the water has dissolved and removed more easily the soluble carbonate of lime than it has deposited the less easily soluble silica, an expression, which, from the point of view taken here, is simply equivalent to saying, that the amount of silica in the waters of solution was insufficient to fill the space occupied by the calcite. Subsequent crystallization of silica within these hollows would simply produce drusy surfaces on a crystalline texture of interlocked crystals. Fossils also undergo so-called secondary replacement, when their forms become distorted and rough, and little circular monticules of silica are distributed over and through their shells and skeletons. This "orbicular silica"

(Beckite markings) is customarily assigned to the later periods of the fossils change, whereas the intimate replacement of the microscopic structure took place in the earliest stage of its inhumation.

In the Trenton limestone of Wisconsin, a more or less magnesian rock, holding from one to three per cent. of soluble silica, the molluscan forms are replaced by silica, forming hard brittle pseudomorphs of much beauty ; and in the Trenton beds of Tennessee we find the corals frequently or universally silicified by secondary silicification (*Columnaria*, *Tetradium*, etc.). It would seem that the silicification of fossils, where it is of a minute and very accurate character, must have been begun before the consolidation of the limestone itself, and have been completed before the layers assumed their final lithological state. But some peculiar instances of an apparent progressive silicification continuous with the weathering of the enveloping rock, are known as where, in the Niagara limestone in western New York, fossils appear in relief above the surface of the dissolved limestone, and are seen to be complete siliceous replacements, the parts of the same fossils, or other similar fossils, enclosed within the rock a short distance below its surface, being entirely dissolved when placed in acid, evincing their calcareous nature. If this is true, the replacement must take place from the soluble siliceous constituents of the rock, which are slowly introduced into the calcareous tests and frame-work of fossils as these are dissolved in carborated waters. It would seem more likely, in most cases, as in the very siliceous and ferruginous Schoharie grit,¹ that silicification has been already partially effected, and that the action of natural solvents is to remove the associated calcareous particles and leave the siliceous residue as the representative of the fossil, somewhat less

¹ In this formation the shells of fossil bivalves are often removed by solution, being almost entirely carbonate of lime; and the siliceous filling, colored brown by the ferruginous oxydation, remains as casts of their interiors. But in other cases silicification has partially replaced the shells, and fragments of these taken from unweathered portions of the rock show upon solution in acid siliceous scales, which remain undissolved. In the Trenton of Tennessee the weathered siliceous shell of gastropods is continuous with the siliceous parts yet plainly seen imbedded in the unweathered limestone.

dense in texture, but a substantial and complete form. In fact, in the case of many specimens of weathered fossils, where the siliceous shells project in high relief above the limestone matrix, the surfaces of the shell are finely perforate, or small holes occur, as if the limestone had been removed from these spaces and the intervening areas of silica remained imperfectly continuous. Silicification seems to have gone on with great energy and completeness in some beds in the same formation in which other beds show but imperfect traces of its action, and this may be ascribed to a greater proportion of soluble silica, and perhaps as well to the presence of organic structures more susceptible to siliceous replacement. As regards the first course, it is true that mere excess of a quartzose matrix does not necessarily facilitate silicification, as we see in the Oriskany sandstone, which is so frequently characterized by cavities from which fossils have been dissolved by carbonated waters, though each one of those cavities is surrounded by sandstone. The extraction of this silica could not in this case be effected so as to replace the calcareous parts of the dissolved fossils, because of its insoluble nature. Soluble silica, that colloidal form which is more readily taken in solution, must be provided, for the substitution of the lime portions of fossils. As regards the second cause, it seems certain that thin and delicate tests or structures, as the septa and tabulæ of corals, the partitions and walls of bryozoans, and the fibrous texture of some brachiopodous shells are more susceptible to replacement by dissolved silica than the valves of lamellibranchs or the whorls of gastropods.

Sorby has called attention to an interesting siliceous replacement in the calcareous grit below the coralline oolite in England, where very small reniform bodies occur, converted into agate or presenting microscopic geodes, whose interior walls were lined with an agate film. Sometimes these reniform bodies are filled with calcareous spar, and these contrasted fillings are seen in the same slide side by side. Whatever these enigmatical bodies really are (Sorby was inclined to regard them as foraminiferous), they illustrate the minute way in which silicification acts, for they are on an average about $\frac{1}{200}$

of an inch in diameter, which would give nearly three million in a cubic inch. In the perforated walls of the favosite corals, where the entire skeleton of the fossil has become silicified, the minute pores are sometimes surrounded by little siliceous mammæ, which seem to have gathered under the influence of a form of concretionary concentration.

The peculiarities of preservation of the delicate internal appendages of brachiopods varies extremely, and while specimens of the same genus or species from one locality refuse to disclose their loops or spiral arms to the paleontologist, those from another, even with indifferent care and easier methods, are readily examined. Thus, the Devonian *Centronella* from England afforded imperfect preforations of the loop, etc., to the Rev. Mr. Glass, even with excessive nicety of treatment, whereas those from Michigan, by simply fracturing them in different directions, established the accuracy of Prof. Winchell's descriptions. In alluding to this Dr. Davidson says, "ordinarily by this process no certain result can be obtained, and none could be obtained in this manner from our Devonian specimens of the same genus. But in these (the American) specimens of *C. Julia* there is sufficient contrast between the color of the loop and the surrounding matrix to make the different parts of the loop very clear when revealed opaquely and by fracture. In most of the specimens the loop is of a rusty-brown color surrounded by a lighter matrix." Again, the *Athyris* of our Devonian is apt to be filled with a dark spar, which, being impervious to light, yields unsatisfactory results, whereas those of the English Carboniferous are filled "with a spar beautifully transparent and peculiarly favorable for working." This is by no means universal, as Prof. Whitfield has displayed the spires of *Athyris spiriferoides* in exquisite perfection in the Hamilton slate specimens. It is singular that, as stated by the Rev. Mr. Glass, the English fossil brachiopods never—or very rarely—exhibit a silicification of the spires in a calcareous matrix, whereas this frequently occurs in the United States, rendering the development of these delicate appendages comparatively simple, and incomparably beautiful.

Few organisms are provided with a siliceous frame-work, and except the radiolarians and the sponges animal life has

limited its process of universal secretion to creating skeletons and coverings of carbonate of lime, in which there has also been mingled in many instances phosphates and occasionally corneous layers of an indeterminate mineral and organic character. Most of the fossils we are required to study originated in calcareous bodies, and were originally deposited as such, and for the most part they as fossils retain their calcareous substance to-day. A mineralogical change, however, has in many cases supervened, and the carbonate of lime, known as aragonite, which formed many shells when occupied by their living tenants, has become changed to the more stable form of the same salt, calcite. This change has been often hastened by pressure and heat, and even, perhaps, by perturbations of the earth's crust, which have reassorted the molecular units and brought them into the secondary state of equilibrium known as calcite. Sorby has shown that the calcareous portion of organisms is at first deposited in the form of granules of variable size. These "afterwards undergo more or less of crystalline coalescence. In some cases this scarcely occurs at all; but in others it does to a very considerable extent during the life of the organism, and this produces a great difference in the character of the particles into which it is resolved by decay. The falling to powder that then takes place is the result of the oxidization and removal of the organic portion, and, if no crystalline coalescence had occurred, the shell or other body might be resolved into the very minute ultimate crystalline granules; whereas, if much coalescence had taken place, it would break up into much larger ones, showing in many cases its minute structure." These observations were made with reference to the condition of the shells of *Lymnæa* and other fresh water molluscs in marls, but doubtless apply to the shells of marine formations, and may explain the fragmentary state of shells in limestones, while it points to an agency in preparing the calcareous mud in which they are embedded, though this latter arises more generally from partial solution of shells in carbonated water. A remarkable form of replacement occurs in calcareous fossils, as it has been shown by Zittel, Hinde and Sollas that the soluble silica of the siliceous skeletons of the

flinty sponges is removed, and its place taken by carbonate of lime, or by oxide and sulphide of iron. The secondary character of this lime seems also proven by the fact that it is always crystalline, and its crystals are placed confusedly in all directions, and not in one, or, as it is technically expressed, are *unoriented*.

Prof. Nicholson, in his study of certain obscure organisms known under the general designation of Stromatoporoids, has indicated three different conditions or phases of their preservation. These organisms are in the main calcareous encrusting or turbinate masses, built up by a succession of poriferous sheets or laminae, between which irregular spaces extend, furrowed by inosculating canals. In the first state of preservation, instanced by this author, the actual calcareous skeleton is preserved, and all cavities are infiltrated with transparent calcite, the skeleton then appearing as a brown granular or cloudy non-crystalline body. In the second method of fossilization more or less silicification has taken place, the cavities becoming solidly silicified and the skeleton remaining calcareous, or the skeleton irregularly presenting a complete siliceous frame-work. In the third method the specimens are preserved in limestones or in argillaceous deposits. The skeleton became infiltrated with fine mud or argillaceous sediment, and was dissolved out, being the less stable form of carbonate of lime—aragonite—and was replaced by calcite. Thus, the skeleton appears as clear as calcite, while the chambers, pores and canal-system of the fossil are represented by comparatively opaque calcareous mud or fine argillaceous fillings. In the skeletons and hard parts of living invertebrates the following distinctions of mineral composition have been determined :

The calcareous foraminifera are composed of calcite, with some aragonite.

The true corals are composed almost entirely of aragonite.

The alcyonarians are for the most part composed of calcite, with small amounts of aragonite and phosphate of lime.

The echinoidea are essentially formed of calcite.

The annelids are enclosed frequently in tests, tubes, or shells made of calcite.

The hard parts, exoskeletons, of crustacea contain varying intermixtures of calcite and phosphate of lime.

The bryozoans have cases composed of a mixture of calcite and aragonite.

The brachiopoda have shells composed of calcite and some phosphate of lime, the latter salt being almost limited to the shells of the inarticulate division of this class—*lingula cranio discina*, etc.

In the lamellibranchs there is found some variation in the composition of shells of different genera, in some the shells are wholly aragonite, in oysters and scollops (*Ostrea*, *Pecten*) the shells are calcite, whereas in mussels *Mytilus* and *Pinnas*, the outer layer is calcite, the inner aragonite.

SOME MANITOBA CLADOCERA, WITH DESCRIPTION OF ONE NEW SPECIES.¹

By L. S. Ross.

No record is to be found among the literature upon Entomostraca, of any systematic work done upon this interesting division of the Crustacea in Manitoba or any of the Provinces of Canada. The region is yet open to the student of the distribution of the group. A short stay in the Province of Manitoba in June, 1895 was utilized by the author in making a few collections from the region about Portage la Prairie on the Canadian Pacific Rail Road fifty-five miles west of Winnipeg. Before leaving the province some vials of alcohol were left with a resident of the town to be filled with collections. A vial was received every second week from the time of the visit until cold weather, the latest being filled Oct. 21, 1895. One vial remained to be filled the following spring.

Collections were taken by the author from the Assiniboin River, from a deep weedy slough which was once the channel of the Assiniboin River, from railroad ditches and from prairie

¹ Read before the Iowa Academy of Sciences, Dec. 1876.